STUDIES ON FLUORIDE REMOVAL KINETICS BY ACTIVATED ALUMINA

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

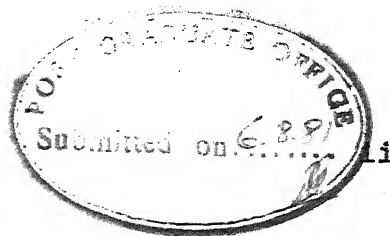## MASTER OF TECHNOLOGY

66890

By

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to the

DEPARTMENT OF CIVIL ENGINEERING

## INDIAN INSTITUTE OF TECHNOLOGY KANPUR

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CERTIFICATE

This is to certify that the present study entitled "Studies on Fluoride Removal Kinetics by Activated Alumina" has been carried out by Shri Satya Prakash Sharma under my supervision and this has not been submitted elsewhere for a degree.

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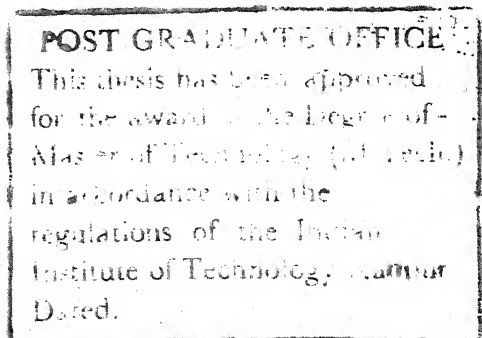
ACKNOWLEDGEMENT

I always cherish my association with Dr. S.D. Bokil.

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I am sorry that my vocabulary is failing to express my acknowledgement to Dr. (Miss) Vijay Lakshmi, but for whose voluntary help, this work would never have been completed.

CONTENTS

LIST OF FIGURES

LIST OF SYMBOLS

d —   Average grain size of activated alumina, mm

$\dfrac{dF}{dt}$ —   Rate of change in fluoride concentration in solution, mg/l/min

F —   Fluoride concentration remaining in solution, mg/l

F_e —   Fluoride concentration in solution at equilibrium condition

F_o —   Initial fluoride concentration

H — HCO_3^- alkalinity, mg/l as $CaCO_3$

K —   Modified first order rate constant^{-1}

p —   pH of the solution

Q —   Difference between initial and equilibrium concentrations of fluoride

q_e —   Adsorption capacity of activated alumina

X_o —   Alumina dose applied to the solution, mg/l

σ —   Ratio of adsorbate to adsorbent.

K_1 —   First order rate constant, minute^{-1}

K_2 —   Second order rate constant, $(mg/l)^{-1} \times minute^{-1}$

t —   Time, minute

ABSTRACT

In the Sixth Five Year Plan provision of rural water supply depends essentially on the availability of ground water resources. In a number of places in the country, the ground water is found to contain excessive concentration of fluoride causing tooth decay. One of the recommended methods of fluoride removal in recent times is adsorption by activated alumina. The work was conducted to study the effects of controlling parameters on the kinetics of fluoride removal using activated alumina.

Batch studies by activated alumina gave results on kinetics of fluoride removal taking into account the grain size, ratio of adsorbate to adsorbent, the pH and bicarbonate alkalinity. It was found that removal was directly dependent on the concentration of fluoride which is over and above the equilibrium concentration. Equilibrium fluoride removal capacity and removal rate were found to be affected by all the above four parameters mentioned. A comprehensive mathematical model was proposed taking into account all the variable parameters.

1. INTRODUCTION AND SCOPE OF STUDY

A very small percentage of Indian population living in urban areas is being served by protected water supplies. In most of the villages, water from well having very poor quality is used for drinking purposes.

The physiological and toxic effects of chemical constituents depend on their concentration. Fluoride is recognised as a normal constituent of natural water and is 17th in the order of abundance of elements on earth's crust.

Fluoride in drinking water may be beneficial or detrimental depending on the concentration. Dental fluorosis is the most common toxic manifestation of excessive fluoride ion in drinking water and is characterized by an increasing mottling of teeth. Higher concentration results in the deposition of calcium fluoride in teeth and bone leading to dental and skeletal fluorosis.

It is now generally accepted that optimum fluoride concentration should be around 1 mg/l. The Manual on Water Supply and Treatment, India (1976) recommends fluoride concentration in drinking water to be 1.0-1.5 mg/l.

Several methods were advocated for removing excessive fluoride from drinking water. They can be broadly divided into two categories - those based upon the addition of some material to the water during the softening or coagulation processes; and those based upon ion-exchange or adsorption processes.

Additive methods include mainly the use of lime, magnesia, calcium phosphate and aluminum sulfate (alone or in combination with a coagulant aid). Such methods were found very uneconomical to bring the fluoride concentration below 10.0 mg/l (Patterson, 1975).

Ion-exchange or adsorption processes recommended the use of processed bone, activated carbon, magnesia, natural and synthetic ion-exchangers, and activated alumina. Among these materials, activated alumina was found to be the most effective and economic adsorbent for fluoride ion removal from drinking water in lower concentration range (Patterson, 1975)

Kinetics of fluoride removal was first studied by Yeun and Anan (1979) using first order kinetic model. It was found that the calculated results were not having good correlation with the reported experimental results as the equilibrium removal capacity was not taken into consideration. Hence it was felt that a model which gives high degree of correlation with experimental values should be proposed, tested and reported. The results presented in this thesis are the attempts made in this direction taking into account the variability of the most important and vital parameters like alkalinity, pH, size of the grain and the ratio of adsorbate to adsorbent on adsorption kinetics of fluoride by activated alumina.

2. REVIEW OF LITERATURE

Fluoride ion is recognized as a normal and frequently occurring constituent of natural waters. The presence of fluoride ion in drinking water is beneficial or detrimental depending on its concentration. Optimum concentrations (0.7-1.2 mg/l) of fluoride in drinking water prevents dental caries in children. However, when drinking water contains excessive fluoride concentration, i.e., as high as 4 mg/l, the teeth of consumers become mottled with a permanent black or grey discolouration. Chronic toxic effects of excessive intake of fluoride ions are usually observed as skeletal abnormalities or damage. The effects range from stiffness and rheumatism to a permanent cripling skeletal rigidity. An increase in the activity of parathyroid glands which regulate metabolism of calcium was observed because of excess fluoride intake. Maximum allowable fluoride concentration in drinking water to prevent dental fluorosis is around 1.5 mg/l. The permissible concentration of fluoride in drinking water is 1.0 mg/l (International Standards, 1963).

2.1 Occurrence

It is reported that in India the fluoride concentration in drinking water exceeds the normally acceptable level in several places, especially in Hyderabad (Daver, 1945), Madras (Raghavachari and Venkataraman, 1940), Andhra Pradesh (Murthy et.al., 1953), Punjab (Khan and Wig, 1945) and in Rajasthan (Thergaonkar and Bhargava, 1974).

Generally surface waters do not exceed fluoride concentrations of 0.3 mg/l unless they are polluted from other sources (Livingston, 1963; Barnett et.al., 1969). Fluoride laden wastewaters are generated from the industries which manufacture pesticides, disinfectants, wood preservatives, metals and glasses. The greatest amount of fluoride discharge into environment may occur during the mining of phosphate rocks, when silicon tetrafluoride is unearthed and released into nearby waters (Yeun and Anan, 1949). The average concentration of fluoride in sea water has been reported to be about 1.35 mg/l (Bewers, 1971). In India, fluoride bearing waters are usually characterized by pH 8.00 $\pm$ 0.50 and 700 mg/l $\pm$ 500 mg/l alkalinity expressed as $CaCO_3$ (Bulusu and Pathak, 1980).

2.2 Defluoridation Methods

Several methods have been devised for removing excessive fluoride from water which can be divided into two categories.

2.2.1 Chemical Additive Coagulation

The chemicals employed in this process include lime, magnesium compounds and aluminum sulfate. The process involves the formation of fluoride precipitates or co-precipitates (Skripach et.al., 1971; Maier, 1972; Miller, 1974). Drawbacks of additive methods are the necessity of additional reagents, higher shipment, treatment cost and large volume of sludge produced.

2.2.2 Adsorption or Ion-exchange Methods

Adsorption methods utilize the passage of water containing fluoride through contact bed (Maier, 1972; Rao et.al., 1975), where fluoride is removed by ion-exchange or by chemical reaction with the adsorbent. The materials used in contact beds include synthetic or natural ion-exchange materials, hydroxyapatite, zeolite, silica gel, sodium silicate, activated carbon and activated alumina.

(a) Ion-exchange materials

Fluoride is removed from water with metal chloride silicate in exchange of chloride ions. The effectiveness of the treatment depends upon the fluoride concentration.

Shtannikav (1961) reported that fluoride can be removed by anion exchange with hydroxide ion. Previous passage of water through the H^+ form of a cation exchange resin increases fluoride removal.

Sastri (1963) prepared cation exchangers from waste materials like paddy husk, tea waste, jute waste and ground nut shell by sulphonation under suitable conditions. It has been reported that these materials remove fluoride from water after treatment with sodium carbonate and alum. Regeneration was accomplished with an alkali but its capacity and costs were not determined.

(b) Hydroxyapatite

The use of bone material for removing fluorides has
long been known and the removal is based on the affinity of
bone for fluorides. This affinity may be explained on the
basis of anion exchange properties of apatites. The carbonate
radical in the apatite comprising bone is replaced by the
fluoride ions in the water and probably fluoride removal is
accomplished by adsorption together with the formation of
fluoroapatite (Alder et.al., 1938; Smith and Smith, 1937).

Some field applications were made using ion-exchange
materials, natural and synthetic hydroxyapatite, but the
plant operation was abandoned since the requirement for the
dose exchange materials and the regeneration chemicals was
high (Smith and Smith, 1937; Swope and Hess, 1937).

(c) Activated Carbon

McKee et.al. (1934) reported that carbon can be used
for the removal of fluoride, but there was no removal of
fluoride until the pH of the solution was reduced to about
3.0.

Bhakuni and Sastri (1963) reported that the activated
carbonized saw dust can be used for fluoride removal and
found the capacity to be 350-450 mg/kg of dry weight.
Seethapathi Rao (1964) demonstrated sulphonated coconut shell
carbon is an efficient defluoridating agent. The defluo-
ridating activity decreases with constant use of carbon
and can be regenerated with 1% alum sulphate (Bhakuni and

Sharma, 1962). The removal mechanism is an ionic adsorption and fluoride forms an insoluble complex with aluminum.

Choi and Chen (1979) observed that activated carbon is not effective in the removal of fluoride, since the sites present on the surface of activated carbon are not fluoride specific.

The removal efficiency decreases with increasing concentration of sulphates for activated carbon. Moreover, fluoride ions have a high affinity for metals, the sites on the surface of non-metallic solids like activated carbon may have a weaker attraction for fluoride than those on the surface of metallic solid viz., activated alumina and activated bauxite. In solutions having high salinity, the activated carbons are not effective for the removal of fluoride.

(d) Aluminum Compounds

Aluminum sulphate and other aluminum salts have been used in combination with insoluble compounds in contact beds or as constituents of floc which is removed by settling and filteration. The fluorides can be removed by the formation of an aluminum fluoride complexes by adsorption on the floc (Boruff et.al., 1937).

Aluminum compounds are relatively inexpensive, easy to use and can be combined advantageously as aids to coagulants such as clays and activated silica. There are methods utilizing aluminum salts in which contact beds of insoluble

material impregnated with aluminum compounds. The data available on the fluoride removal efficiences are insufficient to serve as a basis for estimating costs.(Maier, 1947).

Ferric oxide, chromium borate, mixed oxides of iron and magnesium, bauxite and bog iron ore were also suggested for removing fluorides. However, these materials possess serious drawbacks such as low capacity, difficult or expensive regeneration, high initial cost and lack of selectivity towards the fluoride ion(Maier, 1947).

(e) Activated Alumina

Activated alumina has been extensively used for fluoride removal by many investigators (Fink and Lindsay, 1936; Boruff, 1934). The adsorption capacity of activated alumina in a continuous flow system varied between 6.75 x 10^{-4} g/cm^3 - 11.76 x 10^{-4} g/cm^3 of fluoride.

The effects of physical parameters such as pH and flow rate on removal capacity of the activated alumina were studied by Savinelli and Black (1958). They found that a removal of 7800 g/m^3 was achieved when treated water pH was 5.6. Yuen and Anan(1979) reported maximum removals of 9600 g/m^3 at pH 5 using pure sodium fluoride solution. By suitable control of pH, three pilot plants were able to operate routinely with removal capacities exceeding 4600 g/m^3 and 9200 g/m^3 (Rubel and Woosley, 1979). Moreover, it has been observed by Choi and Chen (1979) fluoride removal efficiency of more than 90% (with an adsorbent dosage of

20 g/l) can be achieved with activated alumina when the initial concentration of fluoride is less than 90 mg/l.

It has been reported that exhausted alumina can be regenerated by a two percent sodium hydroxide solution followed by neutralization of the excess alkali with dilute HCl (Boruff, 1934). It can also be regenerated using dilute solutions of filter alum (Savinelli and Black, 1958). However, Harmon and Kalichman (1965) reported that alum often precipitates out in the bed causing decreased flow rate through the bed and decreased fluoride removal capacity. In order to overcome this problem, Bishop and Sansoucy (1978) used a fluidized activated alumina bed and a capacity of greater than 2.3 kg fluoride/m^3 was achieved with 30-50 mesh media.

Activated alumina is the most effective adsorbent with regard to removal efficiency and removal capacity among all adsorbents tried so far (Choi and Chen, 1979). Moreover, the removal by activated alumina is virtually unaffected by the salinity of other chemical species such as sulphate and dissolved silica.

Earlier studies had shown that initial fluoride concentration had a direct effect on the fluoride removal capacity (Bishop, 1973). This can be attributed to the utilization of less accessible or energetically less active sites because of increased diffusivity and activity of fluoride when initial concentration of fluoride is increased. It has also been observed that pH and alkalinity of water

had a marked influence on removal capacity (Sharma, 1978).
Higher removal capacities were found in waters with low pH
and low alkalinity (Bishop and Sansoucy, 1978).

Adsorption methods are usually appropriate for
relatively low concentrations of fluoride after the bulk
removal by precipitating methods to 10-20 mg/l level
(Patterson, 1975). Although the most likely mechanism for
fluoride removal is adsorption, other mechanisms such as
absorption and precipitation may also occur. The term removal
refers to the total effect of all these possible mechanisms
because it is difficult to separate experimentally the
effect of adsorption, absorption and precipitation.

2.3 Some Special Features of Activated Alumina

2.3.1 Composition

Commercial alumina is prepared by low temperature
($\leqslant 700°$ C) dehydration of aluminum trihydrate and is a mixture
of γ -alumina, some alumina monohydrate and sodium carbonate.
The freshly prepared product is highly active, but tends to
loose activity due to adsorption of water from the surrounding
atmosphere (Heftmann, 1975).

2.3.2 Origin of Surface Charge

It is well known that all interfaces between
water and nonconducting solid surface have a charge arising
from the electrokinetic zeta potential. This is due to
various causes, e.g., ionization of the group in the solid

surface, ordered orientation of solvent molecules at the
interface, or unsaturated charges in the surface structure
of the solid such as those produced by previous mechanical
treatment. This charge is of importance in the adsorption
of ionic solute from water onto alumina (Heftmann, 1975).

The corrundum (alumina) lattice consists largely of
hexagonal closed-packed -alumina, each alumina being
surrounding by four aluminum atoms. This is an ideal system,
which will be disturbed specially near the surface, by
grinding process and abrasion between particles caused by
handling. The crystalline structure will be incomplete in
the damaged areas leaving positively charged aluminum ions
and negatively charged oxygen ions, and the surface will
therefore be in an activated state. Water present in the
surrounding atmosphere, will get ionized after being adsorbed
at the active surface.OH^--groups will therefore be taken
up by Al^{3+} and H^+ will be taken up by O^- sites. Thus both
the actions are producing surface hydroxyl group. Area of
extensive damage will undergo more general hydration to give
$Al(OH)_3$

$$Al_2O_3 + 3H_2O \rightleftharpoons 2Al(OH)_3$$
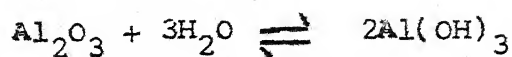
In water, due to polarising effect of neighbouring aluminum
atoms, $Al(OH)_3$ will ionize to give OH^- ion and positive
surface charge

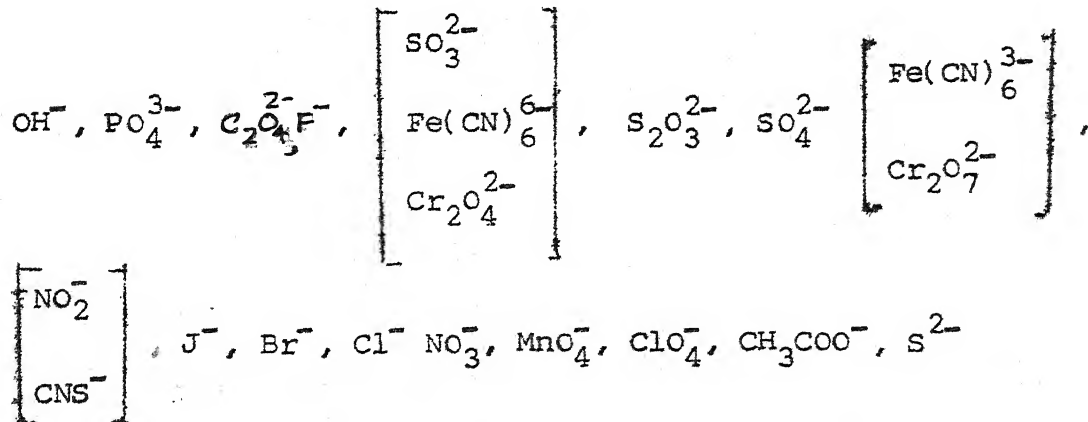$$Al(OH)_3 \rightleftharpoons Al(OH)_2^+ + OH^-$$
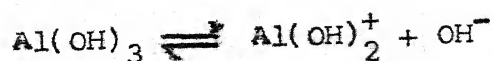
Treatment of corrundum with hydrochloric acid produces a
surface consisting of both covalently bound and ionized
chloride,

$$Al - OH + H^+Cl^- \overset{a}{\rightleftharpoons} \quad Al - Cl + H_2O$$
$$\updownarrow b$$
$$Al^+Cl^-$$
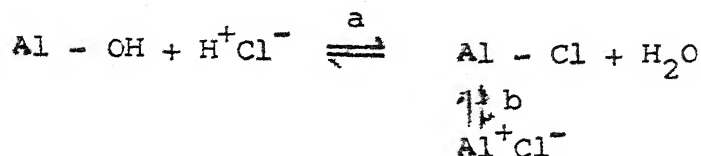
Reaction 'b' is favoured by/increase in acid concentration.
The substrate in this condition will be able to behave as
an ion-exchanger, the chloride ion changing with anion
applied in the solution.

Kubli (1947) found the anion adsorption series of acid
treated alumina in order of decreasing preference.

$$OH^-, PO_4^{3-}, C_2O_4^{2-} F^-, \begin{bmatrix} SO_3^{2-} \\ Fe(CN)_6^{6-} \\ Cr_2O_4^{2-} \end{bmatrix}, \quad S_2O_3^{2-}, SO_4^{2-} \begin{bmatrix} Fe(CN)_6^{3-} \\ Cr_2O_7^{2-} \end{bmatrix},$$

$$\begin{bmatrix} NO_2^- \\ CNS^- \end{bmatrix}, J^-, Br^-, Cl^- NO_3^-, MnO_4^-, ClO_4^-, CH_3COO^-, S^{2-}$$

From the above series it is to be expected that fluoride
removal is adversely affected by the presence of OH^- and PO_4^{3-}
ions.

3. MATERIALS, METHODS AND EXPERIMENTS

3.1 Materials

(a) Activated Alumina: G-80 grade activated alumina was supplied by Associated Cement Companies Limited, India in the form of globules of 5-7 mm diameter. The general properties of activated alumina is given in Table 3.1. These globules were crushed to smaller size particles and sieved through different sieves to get the particles of following sizes.

1. 0.600 - 0.850 mm (Average size = 0.725 mm)

2. 0.425 - 0.600 mm (Average size = 0.512 mm)

3. 0.210 - 0.425 mm (Average size = 0.318 mm)

4. 0.150 - 0.210 mm (Average size = 0.178 mm)

Alumina of each size was then treated with 0.1 N HCl (by keeping alumina in 0.1 N HCl for two hours duration), washed with distilled water and dried at 110°C overnight. Finally it was stored in a closed container for further studies.

(b) Stock Fluoride Solution: 2.210 g of anhydrous sodium fluoride (NaF) was dissolved in distilled water and diluted to 1000 ml (1.0 ml = 1.0 mg F).

(c) Stock Bicarbonate Solution: A very concentrated solution of sodium carbonate (Na_2CO_3) was prepared followed

Table 3.1   General properties of activated alumina*

Surface area, m^2/g	230
Pore volume, cc/g	0.29-0.35
Bulk density (loose), kg/l	0.90
Bulk density (packed), kg/l	1.05
Crushed strength (average point load in kg on 5 mm diameter)	8-12
Loss on attrition, percent	0.3
Water adsorption capacity (wt. %)	
(a) at 15% RH and 30° C	5.0-5.5
(b) at 60% RH and 30° C	14-16
Chemical analysis	
Al_2O_3, percentage	93.0
Na_2O, percentage	0.7
Fe_2O_3, percentage	0.1
SiO_2, percentage	0.1
Loss of ignition (at 1100° C) %	6.0

* Information supplied by Associated Cement Companies Limited, Bombay.

by treatment with 0.1 N HCl to bring down the pH of the solution below 8.4 where only HCO_3^- alkalinity exists. Then it was diluted to such an extent, so that strength of the solution became as 1 ml ≡ 2 mg of HCO_3^- alkalinity as $CaCO_3$.

3.2 Methods of Analysis

3.2.1 Estimation of Fluoride

Fluoride was estimated using alizarin photometric method according to Standard Methods (1965). Calibration curve was prepared by dissolving appropriate quantities of standard fluoride solution (10 ml of stock fluoride solution was diluted to 1 litre with distilled water) to 100 ml with distilled water in the range of 0.00 to 2.50 mg/l. 5 ml of alizarin red solution and 5.0 ml of zirconyl acid reagent were added. Optical density of these samples were measured after 60 ± 2 minutes at the wavelength (λ) = 530 mμ using SYSTRONICS Spectrophotometer. The curve is given in Figure 3.1.

3.2.2 Measurement of pH

pH of the sample was measured by expanded scale pH meter, type 331 model, SYSTRONICS.

3.2.3 Estimation of Other Ions

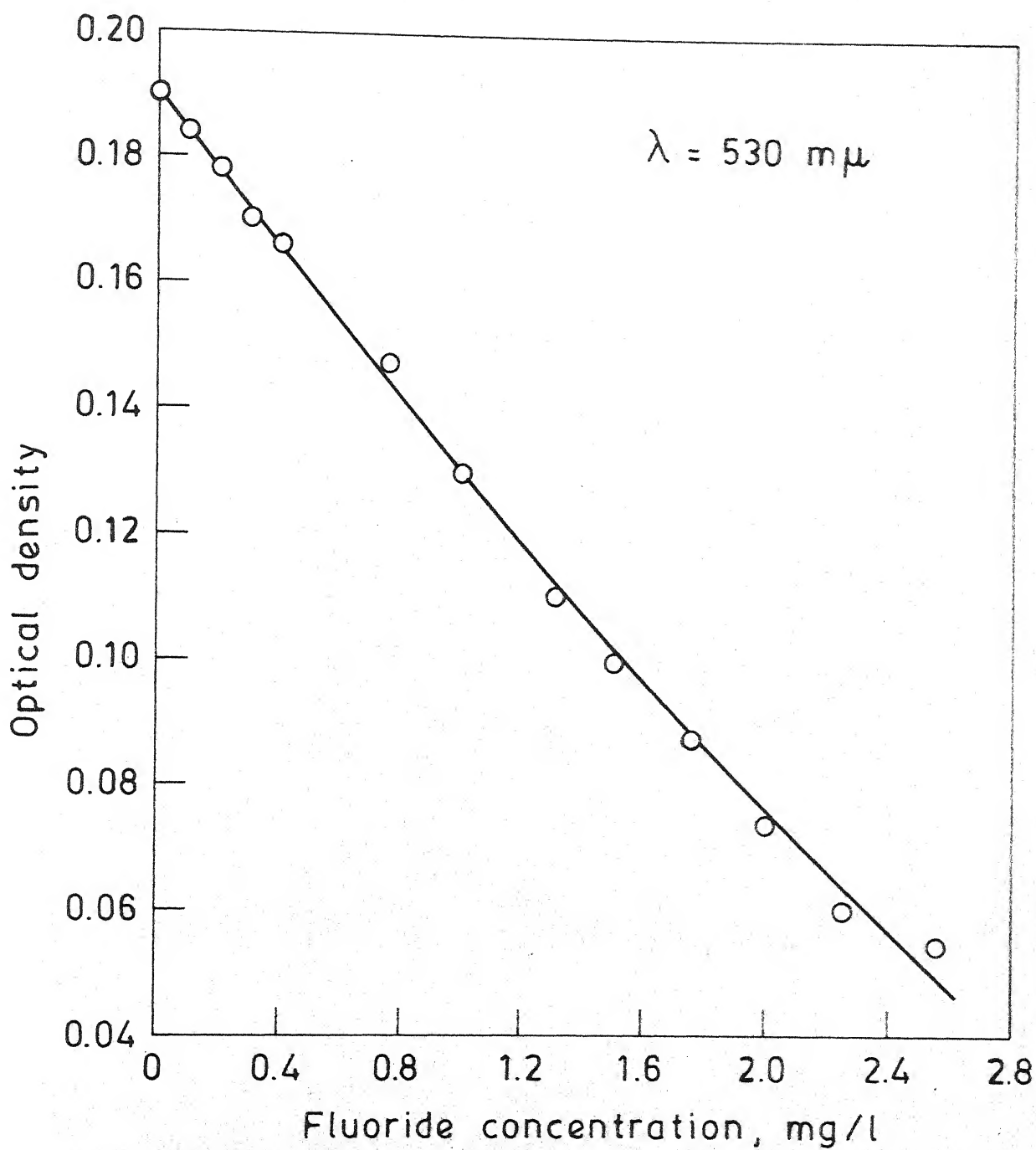All other ions such as CO_3^-, HCO_3^-, etc. were estimated according to Standard Methods (1965).

Fig. 3.1- Standard curve for fluoride determination at 28°C.

3.3 Experiments

Some preliminary studies were conducted to find out the suitable amount of activated alumina of each size, initial fluoride concentration and time duration for performing the kinetic experiments in the prescribed batch reactor (i.e., 500 ml Erlenmeyer flask). All the kinetic studies of fluoride removal were carried out in a continuously stirred batch system only

3.3.1 Basic Kinetic Experiment

250 ml of fluoride solution (20 mg F/l) was taken in the batch reactor and 500 mg of activated alumina (average size 0.318 mm) was added. The reactor was agitated on a wrist shaker to ensure thorough mixing of the solution at room temperature ($28 \pm 2°C$). Then 1.0 ml aliquot was taken at different time intervals (i.e., 0, 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes) and residual fluoride concentration of the supernatant was estimated.

Fluoride solution used in the above experiment had pH 6.3 and alkalinity 4.0 mg/l as $CaCO_3$ (same as of water).

In all other experiments only one parameter was varied to study its effect on the fluoride removal rate and capacity of activated alumina. Other parameters were constant as in the above basic kinetic experiment.

3.3.2 Effect of Grain Size

Effect of grain size on fluoride removal was studied by using 500 mg of activated alumina in a reactor containing 250 ml fluoride solution (F_o = 20 mg/l) under conditions described earlier.

3.3.3 Effect of σ (Ratio of Adsorbate to Adsorbent)

'σ' can be expressed as F_o/X_o, where F_o is initial fluoride concentration in mg/l and X_o is alumina dose in mg/l.

In this study 'σ' was varied by changing F_o only. Five different initial concentrations, F_o (5, 10, 20, 32, 50 mg/l) were taken and kinetic experiments were carried out for each fluoride concentration keeping all other parameters same as in basic kinetic experiment.

3.3.4 Effect of pH

Nine samples (250 ml) of fluoride solution (20 mg/l) were adjusted to different pH values (2.35, 3.6, 4.5, 5.6, 6.5, 7.3, 8.4, 9.2 and 10.0) with 0.1 N HCl and 0.1 N NaOH. 500 mg of activated alumina (size 0.315 mm) was added to each sample and then kinetic experiments were performed for individual sample in the similar way.

3.3.5   Effect of HCO_3^--Alkalinity

5.0 ml of stock fluoride solution (1.0 ml = 1.0 mg F) was taken in six different reactors. Varying amounts of bicarbonate stock solution (1.0 ml = 2.0 mg HCO_3^- as $CaCO_3$) were added to these reactors and the volumes of the solutions were made 250 ml with distilled water so that HCO_3^-- alkalinity in the reactors varied as 0, 80, 100, 240, 480 and 800 mg/l as $CaCO_3$. 500 mg of activated alumina (size 0.315 mm) was added to each reactor and kinetic experiments were performed for individual samples.

4. RESULTS AND DISCUSSION

All the results are represented in graphical form and discussed after each part of the experiment.

It was observed from the preliminary studies that 500 mg of activated alumina of all sizes, 5-50 mg/l initial fluoride concentration and two hour time duration were found suitable for conducting further kinetic experiments in the prescribed batch system.

4.1 Basic Kinetic Experiment

In this experiment, concentration of fluoride decreased exponentially from 20 mg/l to 11.5 mg/l (Figure 4.1). For this type of trend of fluoride removal, the following three types of kinetics were proposed.

4.1.1 First Order Kinetics

It was proposed by Yeun and Anan(1979). According to that,

$$- \frac{dF}{dt} = K_1 F \qquad (1)$$

where,

$\frac{dF}{dt}$ = rate of change of fluoride concentration in solution, mg/l

K_1 = first order reaction rate constant, $minute^{-1}$.

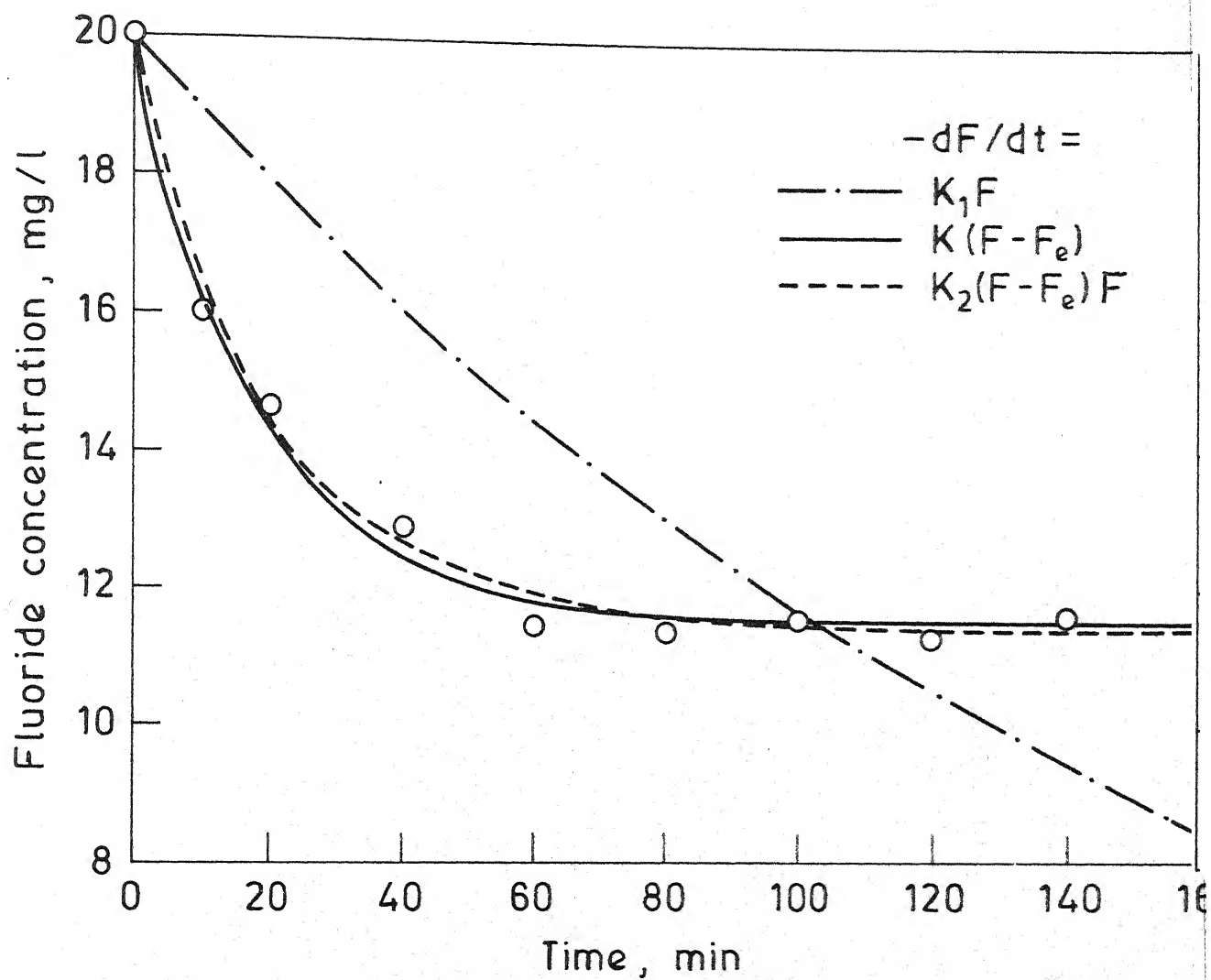F = fluoride concentration remaining in solution after time t, mg/l

t = time, minute

Fig. 4.1 - Kinetics of fluoride removal.

Integrating the above equation w.r.t time and putting the boundary condition (i.e. at $t = 0$, $F = F_o$), we get,

$$F = F_o \, e^{-K_1 t} \tag{2}$$

where,

F_o is initial fluoride concentration in the solution mg/l. This equation gives zero concentration of fluoride after infinite time. It shows that there is no consideration of equilibrium condition in this model. But in actual case as represented in Figure 4.1, there is an equilibrium condition attained after a period of about 80 minutes.

4.1.2 Modified First Order Kinetics

A modified first order kinetic model was proposed to incorporate the equilibrium condition in the present experimental data. According to which, removal rate of fluoride is directly proportional to the fluoride concentration in excess of equilibrium concentration, i.e.

$$-\frac{dF}{dt} = K (F - F_e) \tag{3}$$

where F_e is the equilibrium concentration of fluoride remaining in solution in mg/l and K is modified first order rate constant in minute^{-1}.

Integrating the above equation w.r.t time and putting the boundary condition (at $t = 0$, $F = F_o$), we get,

$$F = (F_o - F_e) \, e^{-Kt} + F_e \tag{4}$$

This model satisfies the equilibrium condition i.e. at $t = \infty$, $F = F_e$ and hence $\frac{dF}{dt} = 0$.

Putting $F_o - F_e = Q$ (5)

equation (4) becomes

$$F = F_o - Q (1 - e^{-Kt})$$ (6)

Here Q gives an idea of adsorption capacity of alumina present in the system. Thus equilibrium adsorption capacity of alumina (q_e, mg Fluoride/g alumina) is given as

$$q_e = \frac{Q}{X_o} \times 1000$$ (7)

where, X_o = alumina dose applied to the solution, mg/l.

In the present study X_o was taken as 2000 mg/l, and hence

$$q_e = \frac{1}{2} Q$$ (8)

4.1.3 Second Order Kinetics

Second order kinetic model was also proposed for the present experimental data as stated below

$$- \frac{dF}{dt} = K_2 F (F - F_e)$$ (9)

where K_2 is second order kinetic rate constant, $(mg/l)^{-1}$ x minute^{-1}.

Integrating this equation w.r.t. time and putting the boundary conditions, we get

$$F = \frac{F_o F_e}{F_o - Q e^{-K_2 F_e t}}$$ (10)

Theoretically, this model seems to be more rational as it takes both the factors into consideration, namely, fluoride concentration and excess fluoride concentration above the equilibrium point at any time.

Best fit curves for the above three models are shown in Figure 4.1, which reveal that first order kinetic model was not applicable to the given experimental data, whereas modified first order and second order kinetic models were very close to the experimental data to the same extent.

Modified first order kinetic model, which is simpler than second order kinetic model, has been used for further studies. In these studies the effect of different parameters i.e. grain size, σ, pH and HCO_3^--alkalinity, was found out on K and q_e.

4.1.4 Determination of K and q_e

In modified first order kinetic model i.e. $F = F_0 - Q(1 - e^{-Kt})$, K and Q are unknown constants, F_0 is a known constant and F and t are variables. So far different values of F and t, best fit model was found out to give the value of K and q_e ($\frac{1}{2}$ Q) using least square technique for a nonlinear regression equation (Kuester, and Mizer, 1973).

Empirical mathematical models of K and q_e were found out as individual functions of each parameter, viz. grain size, σ, pH and HCO_3^--alkalinity. Later on those were combined to give the comprehensive models for K and q_e.

Some arbitrary values of the parameter were chosen to form individual mathematical models as follows

Average grain size, $d = 0.318$ mm, $= 10 \times 10^{-3}$, pH = 6.5 and HCO_3^--alkalinity = 0.0 mg/l as $CaCO_3$.

4.2 Effect of Grain Size

Fig.4.2 shows fluoride removal with time for different grain sizes of alumina. From the best fit curves, it was observed that equilibrium fluoride concentration was decreasing with the decrease in grain size. K and q_e values were computed for all the grain sizes considered and plotted in Fig.4.3.

(a) Effect on K

The value of K decreased linearly with the increase in grain size as follows

$$K = 0.055 - 0.0235 \ (d-0.0318) \qquad (11)$$

where d is average grain size in mm.

As the particle size decreases the number of less accessible sites on alumina surface become easily available to fluoride ions which was reflected in the increase in K value.

(b) Effect of q_e

Value of q_e decreased as the grain size increased (Fig.4.3) and this relationship is governed by the following equation

$$q_e = 4.25 \ (\frac{0.318}{d})^{0.2} \qquad (12)$$

As grain size decreased, surface area of activated alumina obviously increased and hence the increase in q_e is expected. Weber (1972) has also mentioned that the increase in removal capacity is the function of the inverse of the diameter of the adsorbent particle.
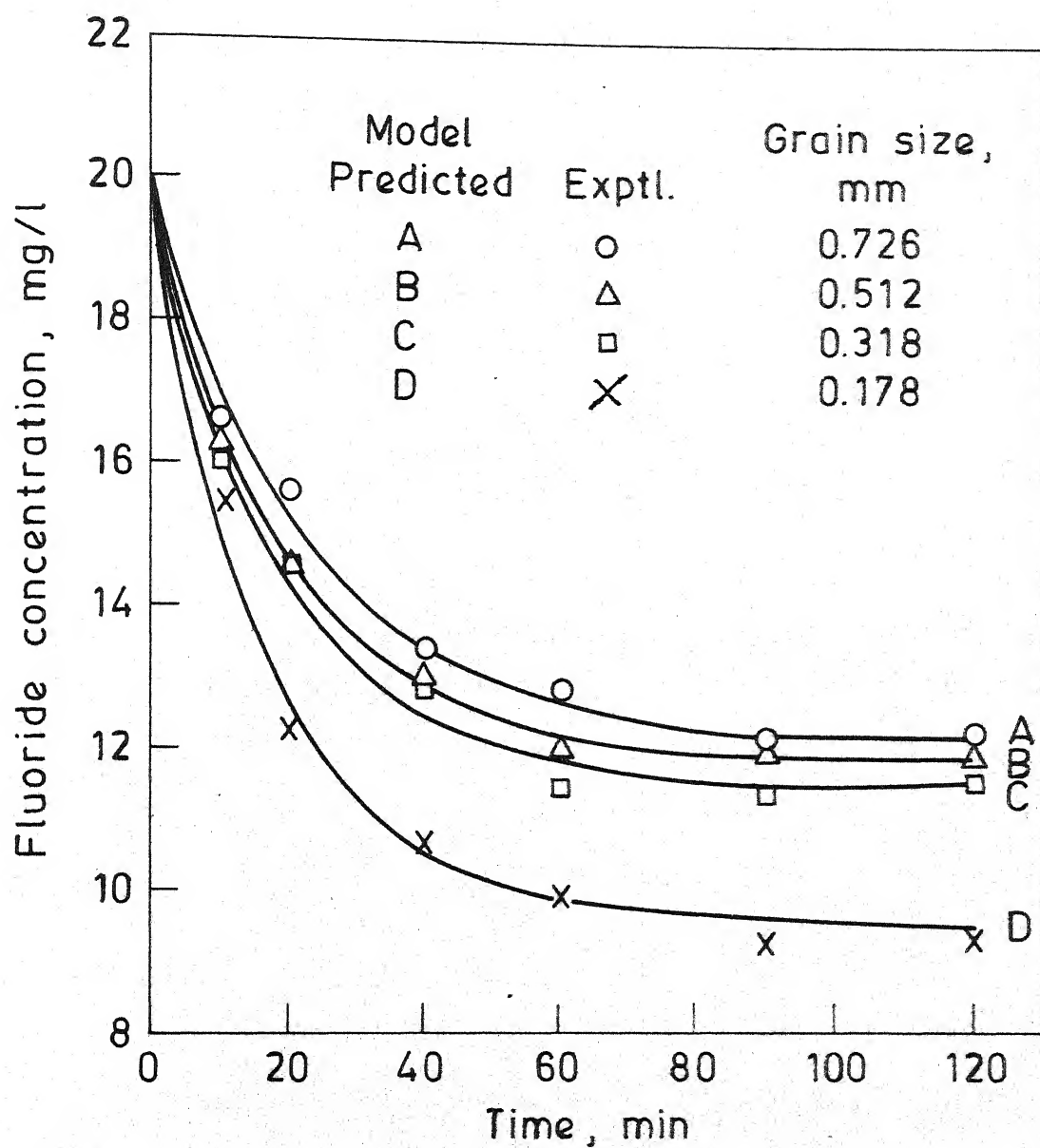
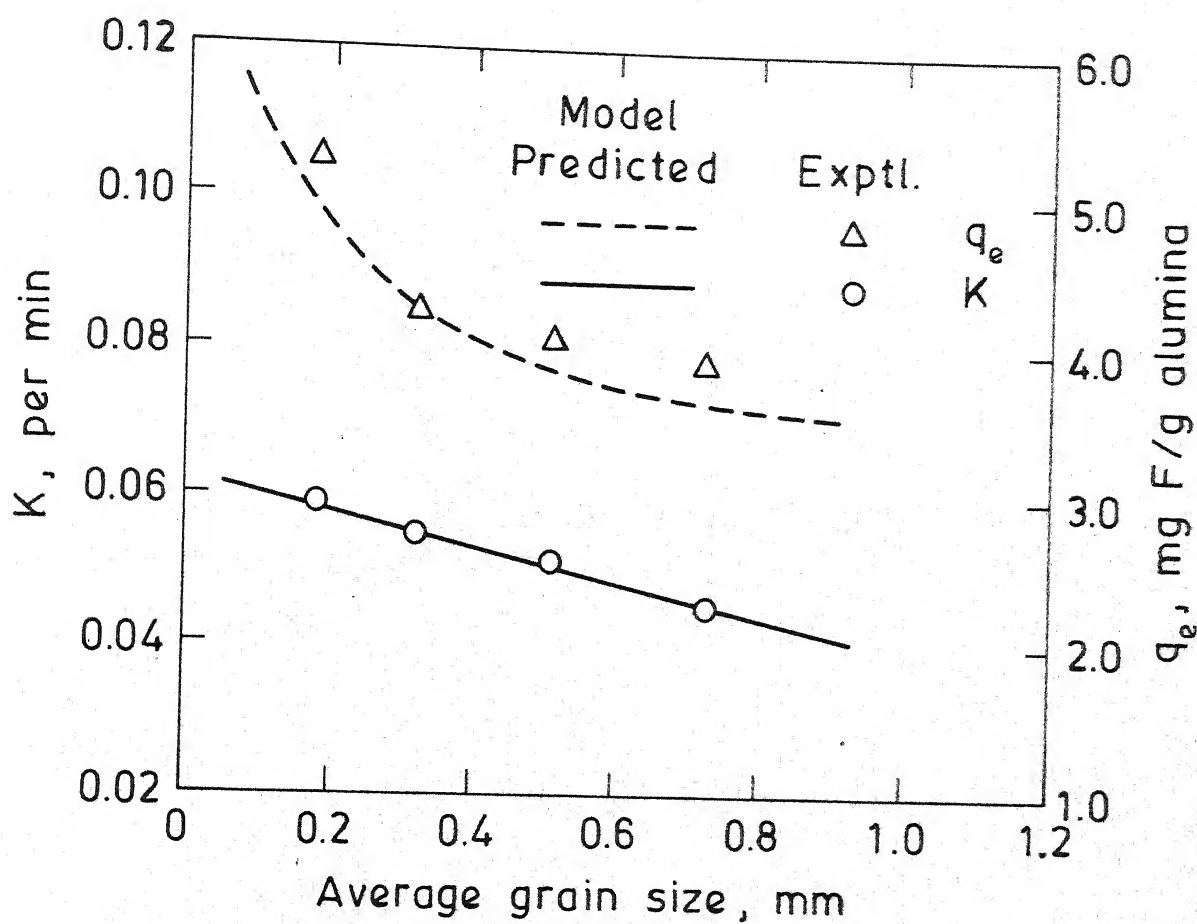Fig. 4.2 - Effect of grain size on fluoride removal.

Fig. 4.3 - Effect of grain size on K and q_e.

4.3   Effect of σ $\left(\dfrac{F_o}{X_o}\right)$

Fig.4.4 shows fluoride removal with time for different values of σ. K and q_e values for these σ values were calculated and plotted in Fig.4.5.

(a) Effect on K

The value of K increased as σ value increased and the behaviour is expressed by following equation

$$K = 0.055 \, (100 \, \sigma)^{0.84} \qquad (13)$$

This behaviour may be due to the high fluoride concentration which is the main driving force for transfer of fluoride ion from solution onto adsorbent.

(b) Effect on q_e

q_e also increased first rapidly and then rate of increase declined as σ increased. The behaviour is governed by the following equation

$$q_e = 4.25 \, \frac{1 - e^{-137.3\sigma}}{0.75} \qquad (14)$$

There was no significant increase in q_e when the value of σ was increased beyond 25×10^{-3}. This may be due to the fact that as fluoride ions increase less accessible sites on alumina surface are also occupied giving an increase in q_e.

4.4   Effect of pH

Fig.4.6 shows fluoride removal with time at different pH values. From the best fit curves, the value of K and q_e were computed and plotted in Fig.4.7.
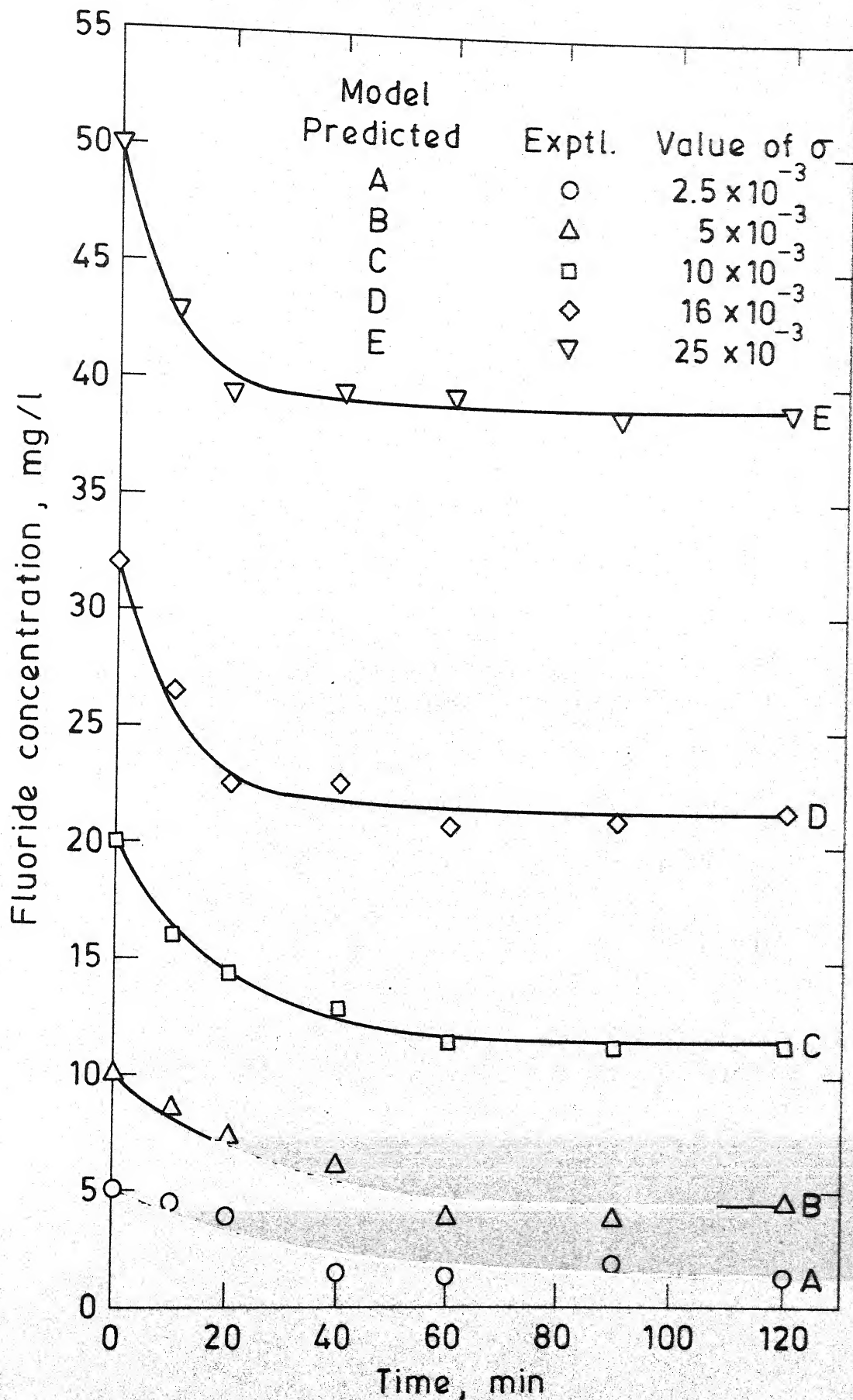
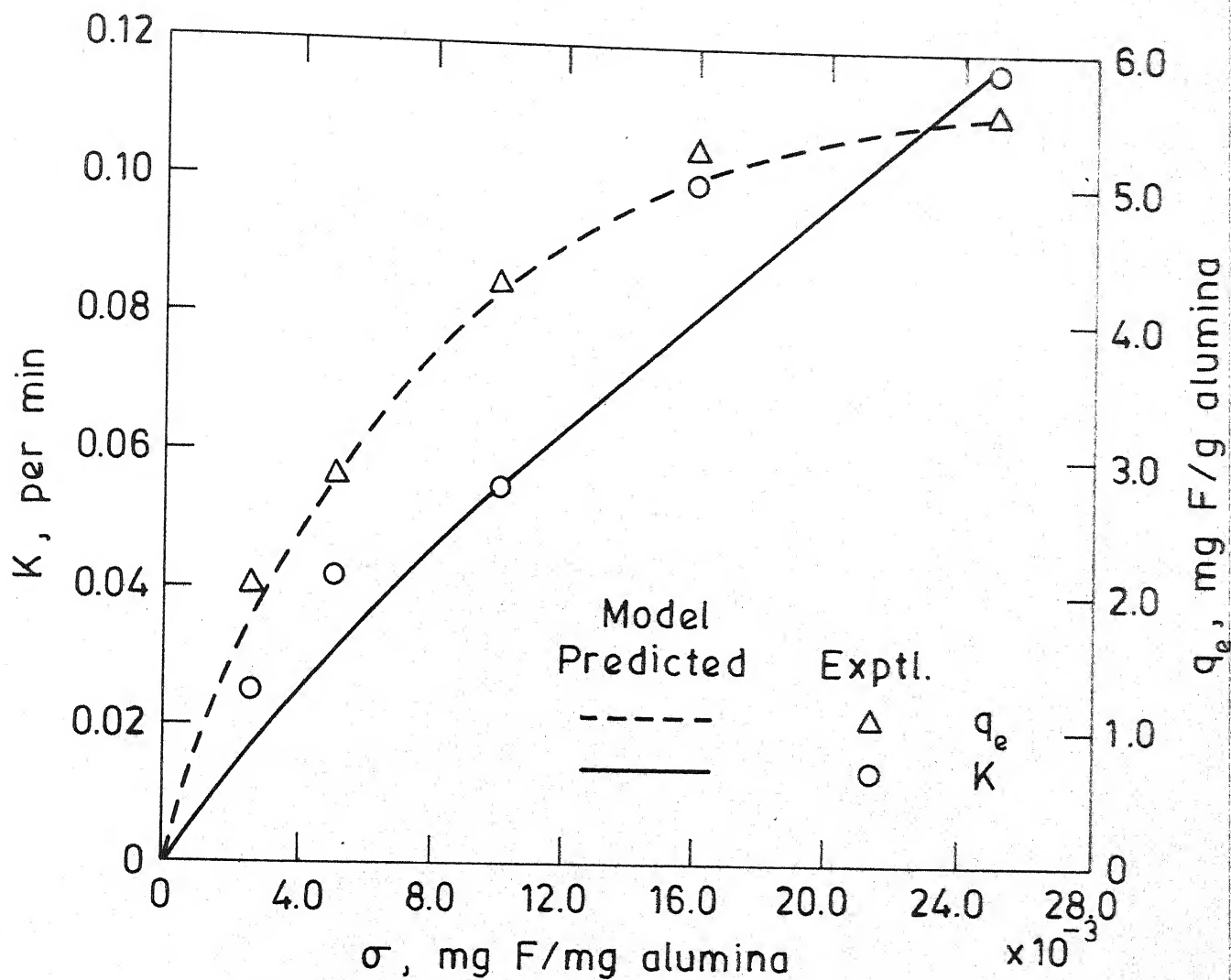Fig. 4.4 - Effect of σ (F_0/X_0) on fluoride removal.

Fig. 4.5 - Effect of σ on K and q_e.

(a) Effect on K

Fig.4.7 shows the actual behaviour of K with respect to pH changes. The behaviour is governed by the following equation

$$K = 0.055 + 0.039 \left(0.985 - e^{-0.376(P - 6.7)^2}\right) \qquad (15)$$

where p is denoted for pH of the solution.

The value of pH corresponding to the minimum K value (0.053) was found to be 6.7. The K value can vary from 0.053 to 0.08 in natural water as pH of natural water varies from 6.5 to 8.4. In acidic range   K-pH plot can be explained on the basis of OH^- ion activity. At lower pH, the OH^- ions adsorbed already on the alumina surface get neutralized and hence competition due to the OH^- ions is minimized which can be reflected by the increase in K value. The explanation for the behaviour of K in basic range of K-pH plot is not known yet.

(b) Effect on q_e

The q_e value decreased linearly as pH was increased and this behaviour is expressed as

$$q_e = 4.25 - 0.514 (p - 6.7) \qquad (16)$$

This can also be explained on the basis of OH^- ion activity. As the pH goes down the more number of sites on alumina surface, already occupied by OH^- ions, become free to be occupied by Fluoride ion. Similar trend was observed by Bishop and Sansoucy (1978).
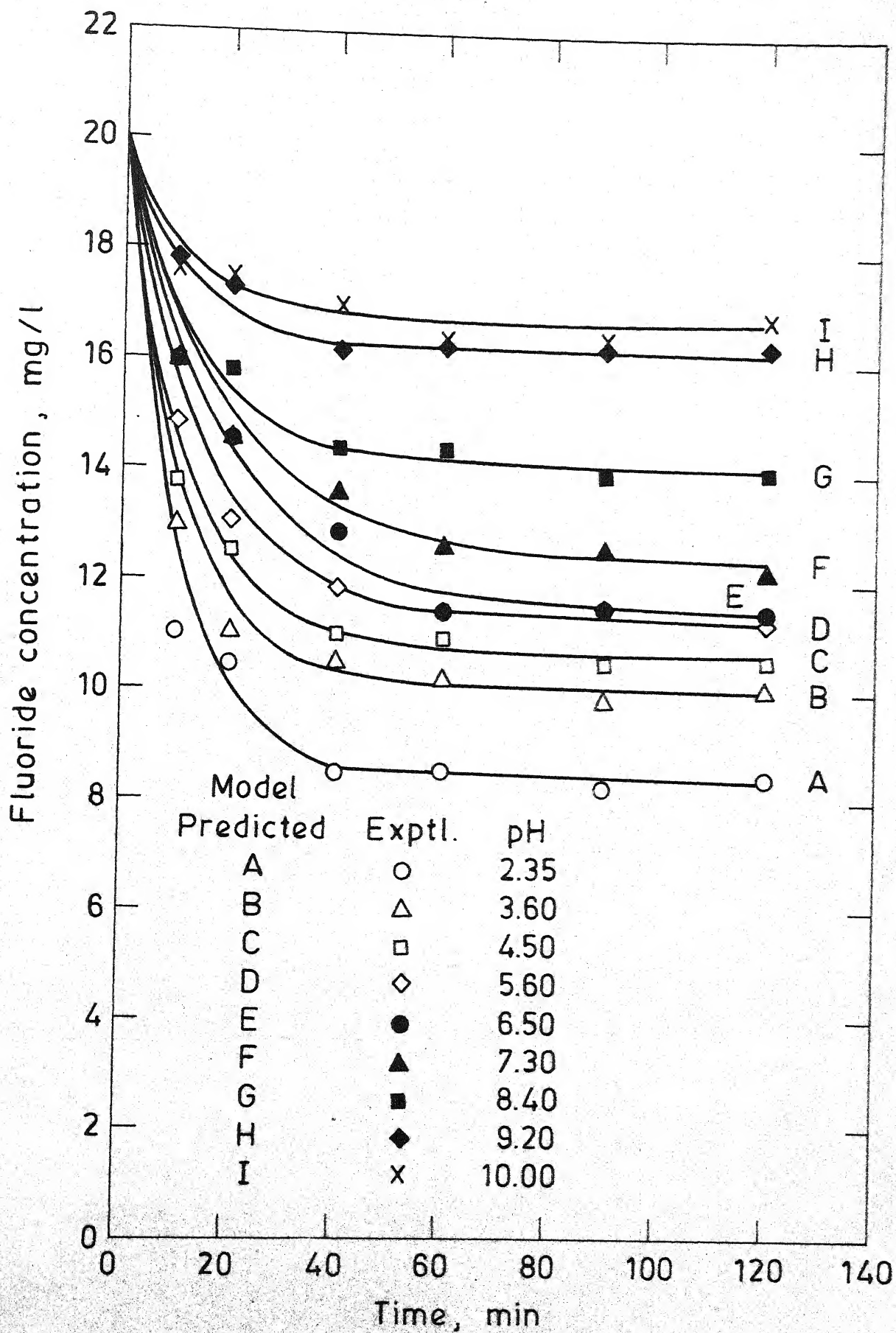
Fig. 4.6 - Effect of pH on fluoride removal.
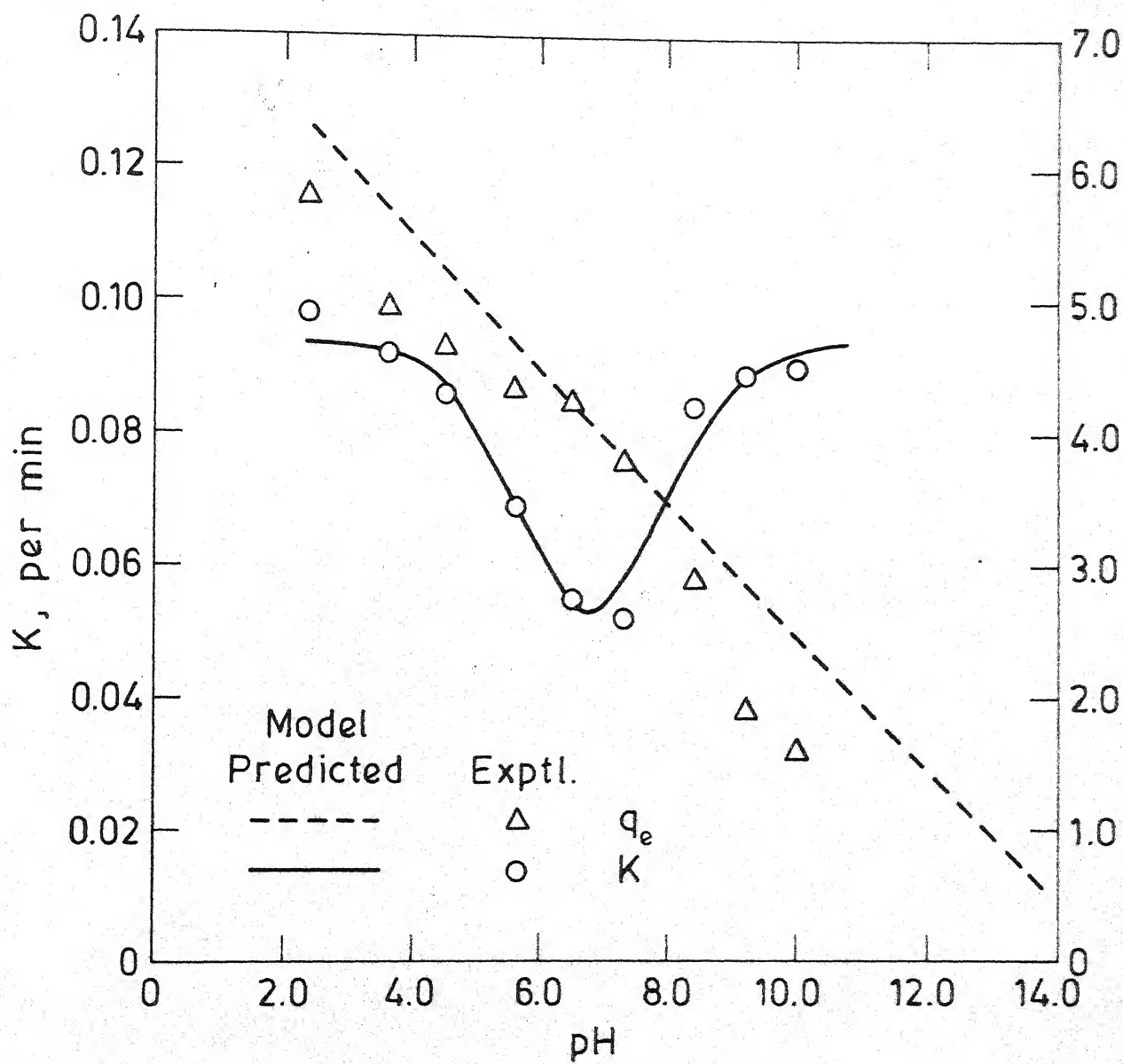
The legend within the figure reads:

Model Predicted	Exptl.	pH
A	○	2.35
B	△	3.60
C	□	4.50
D	◇	5.60
E	●	6.50
F	▲	7.30
G	■	8.40
H	◆	9.20
I	✕	10.00

Fig. 4.7 - Effect of pH on K and q_e.

4.5   Effect of HCO_3^--Alkalinity

Fig.4.8 shows the trend of fluoride removal with time for different HCO_3^--alkalinity values; K and q_e values were computed and plotted in Fig.4.9.

(a)   Effect on K

Fig.4.9 shows the trend of K with HCO_3^--alkalinity, the behaviour was governed by the following equation

$$K = 0.055 + 0.0325\ (1-e^{-4.5 \times 10^{-2}H}) \qquad (17)$$

where H is HCO_3^--alkalinity in mg/l as $CaCO_3$.

(b)   Effect on q_e

The behaviour of q_e in response to HCO^-_3-alkalinity is shown in Fig.4.9 and was governed by the mathematical relationship

$$q_e = 4.25 - 1.49\ (1 - e^{-5 \times 10^{-3}H}) \qquad (18)$$

The computed variation in K and q_e due to change in HCO_3^- - alkalinity of the solution were found to be of the same magnitude as that due to the corresponding pH changes of the solution.

Hence it may be concluded that the adsorption of fluoride ion by the activated alumina is probably not directly influenced by HCO_3^- ion, but is influenced by OH^- ions which are in equilibrium with HCO_3^--ions as follows

$$HCO_3^- \rightleftharpoons OH^- + CO_2$$
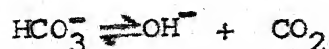
Therefore, for the purpose of comprehensive modelling, the effect of HCO_3^--alkalinity on K and q_e can be omitted as it
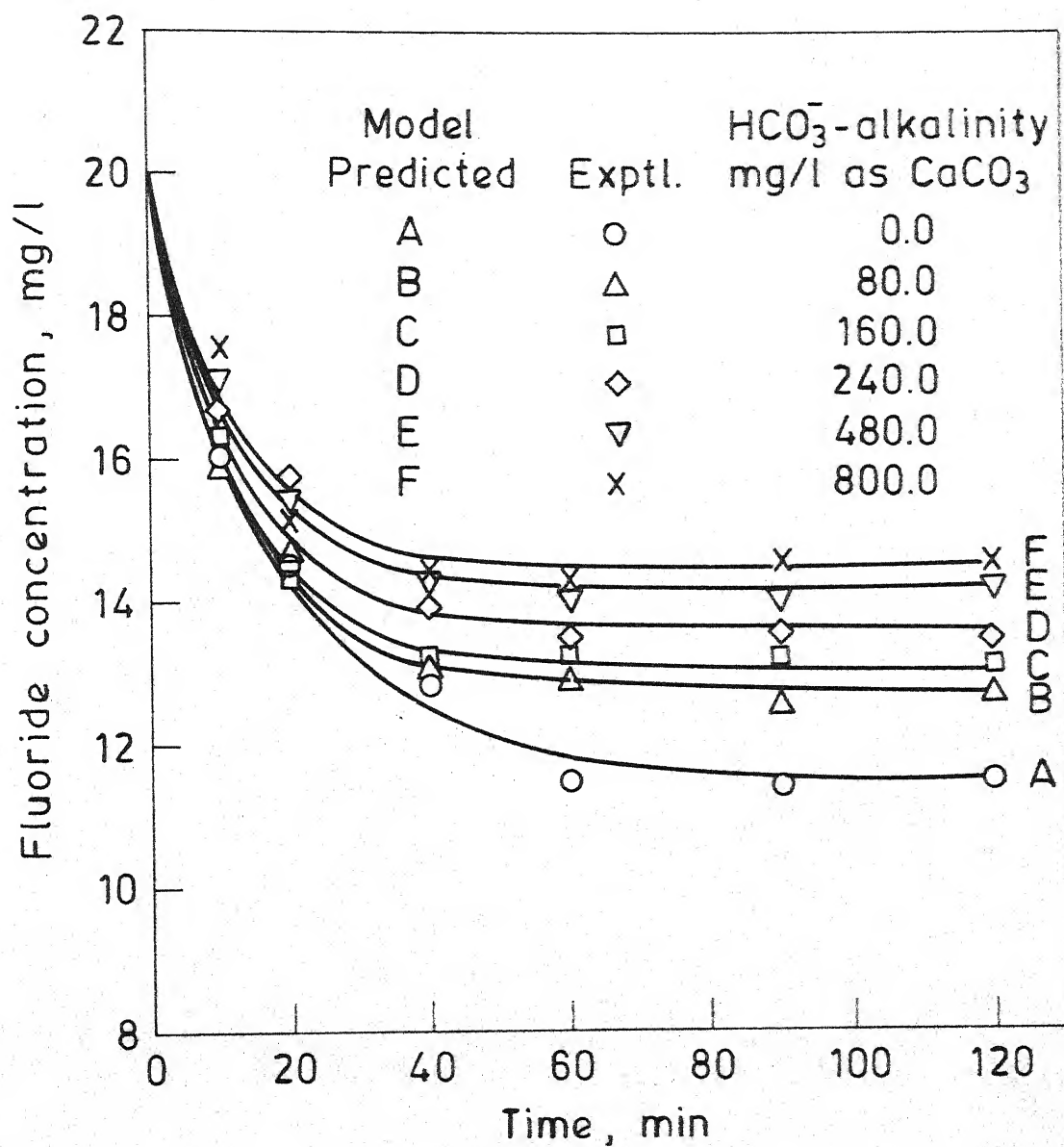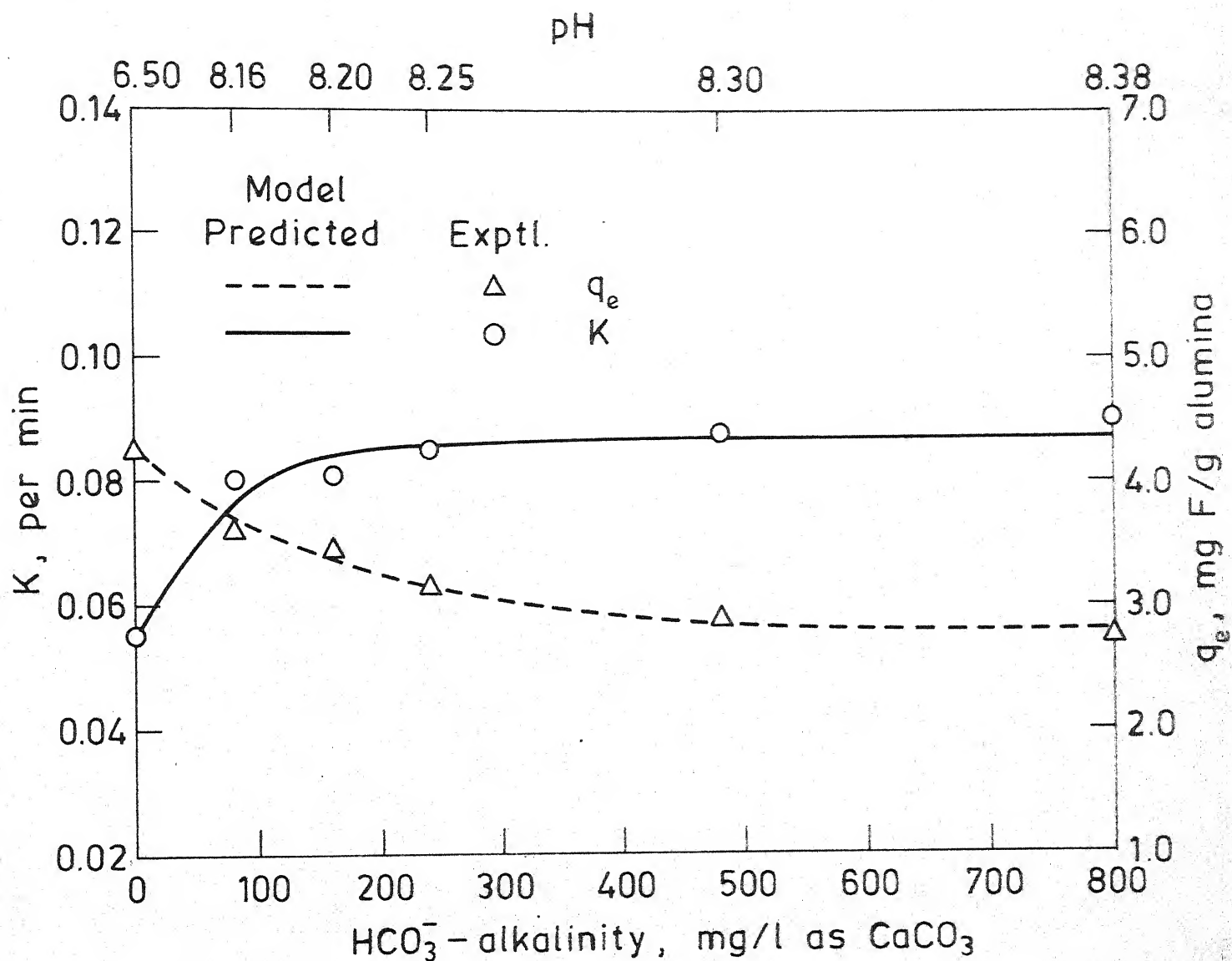
Fig. 4.8 - Effect of HCO_3^- - alkalinity on fluoride removal.

Fig. 4.9 - Effect of HCO_3^--alkalinity on K and q_e.

will be taken into account with pH effect on K and q_e.

4.6 Comprehensive Models for K and q_e

The comprehensive models for K and q_e were obtained by combining all individual models for different parameters in a manner given below

$$K = 0.055 \ (1.14-0.43d)(100\sigma)^{0.845}(1.7-0.7\exp(-9.38(p-6.7)^2))$$

$$\tag{19}$$

$$q_e = 4.25 \ (\frac{0.318}{d})^{0.20} \ (\frac{1 - e^{-137.3\sigma}}{0.746})(1.79 - 0.12 \ p)$$

$$\tag{20}$$

Here $K = 0.035$ minute and $q_e = 4.85$ mgF/g alumina at reference values of the parameters i.e. at $d = 0.318$ mm, $\sigma = 10x10^{-3}$, $p = 6.5$.

Thus the effects of these different parameters were studied w.r.t reference K and q_e values(0.055 minute^{-1} and 4.85 mgF/g alumina respectively).

4.6.1 Testing of the Models

A separate kinetic experiment was conducted to verify the proposed comprehensive models. The results are as follows:

at pH $= 8.5$, d $= 0.318$ mm, $\sigma = 5x10^{-3}$,

observed $K = 0.052$ minute^{-1}, and $q_e = 2.86$ mgF/g alumina,

computed $K = 0.045$ minute^{-1}, and $q_e = 3.26$ mgF/g alumina.

5. CONCLUSIONS

On the basis of the present study, following conclusions have been drawn.

i) Modified first order kinetics is proposed for the removal of fluoride by activated alumina.

ii) Fluoride removal rate (K) and removal capacity (q_e) of activated alumina are found to be effected by pH of the water significantly. Removal rate is minimum (0.053 minute^{-1}) at pH 6.7. For natural waters having pH 6.5-8.5, removal rate varied from 0.053-0.080 minute^{-1}. Removal capacity decreases with an increase in pH.

iii) The ratio of initial fluoride concentration to the alumina dose, (σ), plays an important role in fluoride removal. Increase in removal rate and capacity are observed with an increase in the ratio.

iv) Grain size is an important factor effecting the removal rate and capacity which are decreased with the increase in grain size.

v) It is observed that HCO_3^--alkalinity effects the fluoride removal rate and removal capacity. This effect is thought to be caused by OH^- ions which are in equilibrium with HCO_3^- ions.

vi) Comprehensive mathematical models are proposed for fluoride removal rate and removal capacity of activated alumina incorporating the effects of various parameters studied.

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